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APPLICATION FOR UNITED STATES LETTERS PATENT

Title:

**PHOTORESIST POLYMER AND PHOTORESIST  
COMPOSITION INCLUDING THE SAME**

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## PHOTORESIST POLYMER AND PHOTORESIST COMPOSITION INCLUDING THE SAME

### Technical Field

5                    Improved photoresist polymers and photoresist compositions  
containing the same are disclosed. More specifically, a photoresist polymers and  
photoresist compositions containing the same are disclosed which are useful for a  
photolithography processes using light sources of the far ultraviolet region such as  
EUV (Extreme Ultraviolet, 13nm) during the manufacturing of ultrafine circuits of  
10 highly integrated semiconductor devices.

### Description of the Related Art

                    Recently, in the manufacture of semiconductors, chemical  
amplification-type DUV (Deep Ultraviolet) photoresists have proven to be useful in  
achieving high sensitivity in processes for forming ultrafine patterns. These  
15 photoresists are prepared by blending a photoacid generator with polymer matrix  
having acid labile structures.

                    According to a reaction mechanism of such photoresists, the photoacid  
generator generates acids when it is irradiated by the light source. The main chain or  
branched chain of the polymer matrix in the exposed portion reacts with the generated  
20 acids, and is decomposed or cross-linked so that the polarity of the polymer is  
considerably altered. This alteration of polarity results in a solubility difference in the  
developing solution between the exposed area and the unexposed area. In case of  
negative photoresists, acids are generated in the exposed area, and the main chain or  
branched chain of the polymer compound causes a cross-linking reaction. As a result,  
25 the crosslinked polymer compounds are not dissolved in a subsequent development  
process, thereby forming negative images of a mask on the substrate.

                    In the photolithography process, resolution depends on wavelength of  
light sources. As the wavelength of light source becomes smaller, ultrafine patterns  
may be formed. For exposure equipment required to form patterns of less than 50nm,  
30 EUV equipment is currently under development, and photoresists are also under  
development. When patterns of less than 50nm are formed, the patterns of positive  
photoresists easily collapse. As a result, improved negative photoresists are needed  
which avoid the collapse problem associated with positive photoresists.

## SUMMARY OF THE DISCLOSURE

Accordingly, photoresist polymers and photoresist compositions containing the same are disclosed which are useful for a photolithography process using an EUV light source when ultrafine patterns of less than 50nm are formed.

Processes for forming a photoresist pattern by using the above-described photoresist composition are also disclosed. Semiconductor devices prepared according to the above-described process for pattern formation are also disclosed.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an NMR spectrum of a photoresist polymer obtained from Example 1.

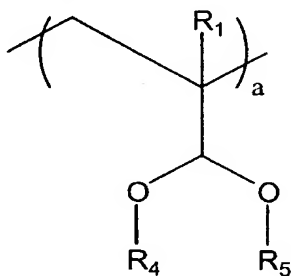
Fig. 2 is a photograph of a photoresist pattern formed using a photoresist composition obtained from Example 3.

Fig. 3 is a photograph of a photoresist pattern formed using a photoresist composition obtained from Example 4.

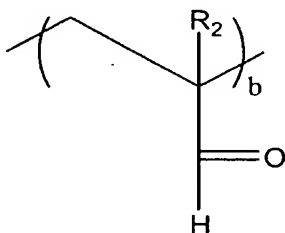
## DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

A photoresist polymer comprises a repeating unit of Formula 1, Formula 2 and Formula 3:

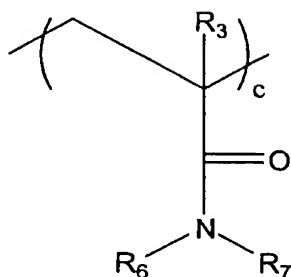
Formula 1



Formula 2



### Formula 3



5

wherein

$R_1$ ,  $R_2$  and  $R_3$  individually are hydrogen or methyl;

$R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$  individually are linear or branched  $C_1$ - $C_{10}$  alkyl;

$a$ ,  $b$  and  $c$  individually are numbers of repeating unit; and

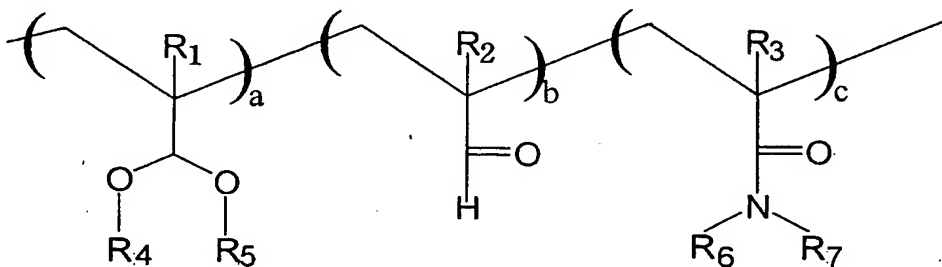
the relative ratio of  $a : b : c$  is in the range of 10~50mol% : 0~30mol%

10 : 50~80mol%.

The molecular weight of the photoresist polymer is 4000~40000.

Preferably, the photoresist polymer comprises a repeating unit of Formula 4:

### Formula 4



15

wherein

$R_1$ ,  $R_2$  and  $R_3$  individually are hydrogen or methyl;

$R_4$ ,  $R_5$ ,  $R_6$  and  $R_7$  individually are linear or branched  $C_1$ - $C_{10}$  alkyl; and

the relative ratio of  $a : b : c$  is in the range of 10~50mol% : 0~30mol%

: 50~80mol%.

20

The photoresist polymer preferably comprises the repeating unit of Formula 4 in amount of at least 10wt% based on the total photoresist polymer.

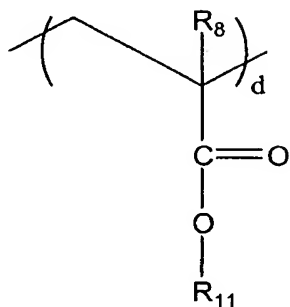
Preferably, the repeating unit of Formula 4 is poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolein).

In addition, there is provided a negative photoresist composition comprising a photoresist polymer described above as a base resin.

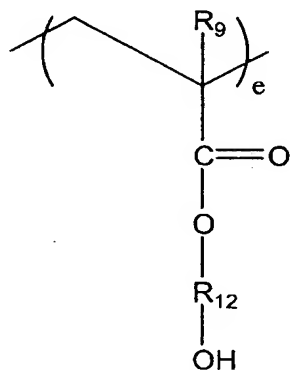
The disclosed negative photoresist composition further comprises polyvinylphenol or a second photoresist polymer comprising a repeating unit of

5 Formula 5, Formula 6 and Formula 7 as the base resin:

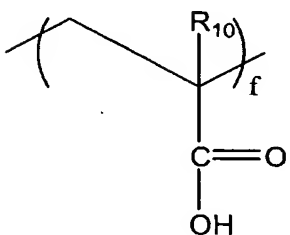
Formula 5



Formula 6



Formula 7



wherein

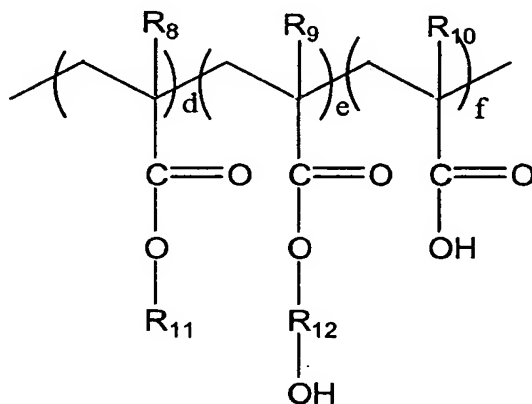
15  $\text{R}_8$ ,  $\text{R}_9$  and  $\text{R}_{10}$  individually are hydrogen or methyl;

$\text{R}_{11}$  is linear or branched  $\text{C}_1$ - $\text{C}_{10}$  alkyl; and

$\text{R}_{12}$  is linear or branched  $\text{C}_1$ - $\text{C}_{10}$  alkylene.

The molecular weight of the second photoresist polymer is 4000~40000. Preferably, the second photoresist polymer comprises a repeating unit of Formula 8:

Formula 8



wherein

R<sub>8</sub>, R<sub>9</sub> and R<sub>10</sub> individually are hydrogen or methyl;

R<sub>11</sub> is linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl;

R<sub>12</sub> is linear or branched C<sub>1</sub>-C<sub>10</sub> alkylene;

d, e and f individually are numbers of repeating unit; and

the relative ratio of d : e : f is in the range of 10~70mol% : 10~50mol% : 10~50mol%.

The second photoresist polymer preferably comprises the repeating unit of Formula 8 in amount of at least 10wt% based on the total second photoresist polymer.

Preferably, the repeating unit of Formula 8 is selected from the group consisting of poly(methylmethacrylate/2-hydroxyethylmethacrylate/acrylic acid), poly(methylmethacrylate/2-hydroxypropylmethacrylate/acrylic acid), poly(ethylmethacrylate/2-hydroxypropylmethacrylate/acrylic acid) and poly(ethylmethacrylate/2-hydroxyethylmethacrylate/acrylic acid).

The disclosed negative photoresist composition comprises blend polymer of poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolein) and polyvinylphenol, blend polymer of poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolance) and poly(methylmethacrylate/2-hydroxyethylmethacrylate/acrylic acid), blend polymer of poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolein) and

poly(methylmethacrylate/2-hydroxypropylmethacrylate/acrylic acid), blend polymer of poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolein) and poly(ethylmethacrylate/2-hydroxypropylmethacrylate/acrylic acid), blend polymer of poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolein) and  
5 poly(ethylmethacrylate/2-hydroxyethylmethacrylate/acrylic acid) or mixtures thereof as a base resin.

The disclosed photoresist composition comprising the above photoresist polymers as a base resin also includes an organic solvent and a photoacid generator.

10 Any of conventional photoacid generators, which may generate acids when they are exposed to light, can be used. Some of conventional photoacid generators are disclosed in U.S. Patent No. 5,212,043 (May 18, 1993), WO 97/33198 (Sep 12, 1997), WO 96/37526 (Nov 28, 1996), EP 0 794 458 (Sep 10, 1997), EP 0 789 278 (Aug 13, 1997), U.S. Patent No. 5,750,680 (May 12, 1998), U.S. Patent No.  
15 6,051,678 (Apr 18, 2000), GB 2,345,286 A (July 5, 2000), U.S. Patent No. 6,132,926 (Oct 17, 2000), U.S. Patent No. 6,143,463 (Nov 7, 2000), U.S. Patent No. 6,150,069 (Nov 21, 2000), U.S. Patent No. 6,180,316 B1 (Jan 30, 2001), U.S. Patent No. 6,225,020 B1 (May 1, 2001), U.S. Patent No. 6,235,448 B1 (May 22, 2001) and U.S. Patent No. 6,235,447 B1 (May 22, 2001). Sulfide type or onium type compounds are  
20 primarily used for the photoacid generator.

Preferably, the photoacid generator is one or more selected from the group consisting of diphenyl iodide hexafluorophosphate, diphenyl iodide hexafluoroarsenate, diphenyl iodide hexafluoroantimonate, diphenyl p-methoxyphenylsulfonium triflate, diphenyl p-toluenylsulfonium triflate, diphenyl p-isobutylphenylsulfonium triflate, diphenyl p-tert-butylphenylsulfonium triflate,  
25 triphenylsulfonium hexafluorophosphate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate, dibutyl-naphthylsulfonium triflate, phthalimidotrifluoromethane sulfonate, dinitrobenzyltosylate, n-decyl disulfone and naphthylimido trifluoromethane  
30 sulfonate. The photoacid generator is preferably present in an amount ranging from 1 to 10 wt% to the base resin. When the photoacid generator is present in the amount of less than 1 wt%, it lowers photosensitivity of the photoresist composition. When the photoacid generator is present in the amount of more than 10wt%, it results in a poor pattern formation due to its high absorption of far ultraviolet rays.

Any of organic solvents, which are generally used in the photoresist composition, can be used. Some of conventional solvents are also disclosed in the documents described above. Preferred organic solvents for the photoresist composition include methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, propyleneglycol methyletheracetate, cyclohexanone, 2-heptanone and ethyllactate. Preferably, the organic solvent is present in an amount ranging from 700 to 4000 wt% to the base resin in order to obtain a photoresist film having a desired thickness.

Processes for forming a photoresist pattern may comprise:

- (a) coating the photoresist composition described above on an underlying layer to form a photoresist film;
- (b) exposing the photoresist film to light; and
- (c) developing the resulting structure to obtain a photoresist pattern.

The process for forming a photoresist pattern can further comprise soft baking before part (b) or post baking after part (b). Preferably, the soft and post baking steps are performed at a temperature ranging from 70 to 200°C.

Exemplary light sources include EUV (13nm), ArF (193nm), KrF (248nm), VUV (157nm), E-beam, X-ray and ion beam. Preferably, the exposure energy ranges from 1 to 100mJ/cm<sup>2</sup>.

Part (c) can be performed with an alkaline developing solution which is preferably TMAH (tetramethylammonium hydroxide) aqueous solution ranging from 0.01 to 5 wt%.

According to mechanism of the disclosed negative photoresist, the photoacid generator generates acids when they are exposed to ultraviolet rays from light sources. In the baking process after exposure, the acids cause cross-linking reaction of the polymer comprising repeating unit of Formula 4 with polyvinylphenol or the polymer comprising repeating unit of Formula 4 with the polymer comprising repeating unit of Formula 8 so that they are not dissolved in the subsequent development process. However, since the cross-linking reaction does not occur in the unexposed area, the polymers are dissolved in the subsequent development process, thereby forming negative images of a mask on the substrate.

A semiconductor device manufactured according to the process described above is also disclosed.



The disclosed photoresist polymers and photoresist compositions containing the same will be described in more details by referring to examples below, which are not intended to be limiting.

Example 1. Preparation of Photoresist Polymer (1)

5 To tetrahydrofuran (300g) were added N,N-dimethylacrylamide (70g), acrolein (30g) and AIBN (2,2'-azobisisobutyronitrile) (5g). The resulting mixture was reacted at 66°C for 8 hours. After reaction, the resulting mixture was precipitated in ether, filtered, and dehydrated, thereby obtaining poly(N,N-dimethylacrylamide/acrolein) (45g).

10 To methanol (1L) were added poly(N,N-dimethylacrylamide/acrolein) (45g) and p-toluenesulfonic acid (0.5g). The resulting mixture was refluxed at 90°C for 24 hours, and concentrated using a rotary distiller.

Then, the concentrated resulting solution was added to normal hexane (2L), and stirred to separate product from ethylether. The ethylether was removed,  
15 and mucous product remained on the bottom of a beaker. The product was dehydrated to obtain poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolein) (see Fig. 1).

Example 2. Preparation of Photoresist Polymer (2)

To tetrahydrofuran (250g) and methylethylketone (250g) were added  
20 methylmethacrylate (40g), 2-hydroxyethylmethacrylate (30g), acrylic acid (30g) and AIBN (2.5g). The resulting mixture was reacted at 66°C for 8 hours. After reaction, the resulting mixture was precipitated in ether, filtered, and dehydrated, thereby obtaining poly(methylmethacrylate/2-hydroxyethylmethacrylate/ acrylic acid) (86g). The polystyrene converted number average molecular weight of  
25 poly(methylmethacrylate/2-hydroxyethyl methacrylate/acrylic acid) was 17,500.

Example 3. Preparation of Photoresist Composition (1)

To propyleneglycolmethyletheracetate (PGMEA) (130g) as an organic solvent were added poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolein) (3g) obtained from Example 1, polyvinylphenol having molecular weight of 8,000  
30 (7g) and triphenylsulfonium triflate (0.05g) as a photoacid generator. The resulting mixture was filtered with a 0.20µm filter, thereby a disclosed photoresist composition.

#### Example 4. Preparation of Photoresist Composition (2)

To propyleneglycolmethyletheracetate (PGMEA) (130g) as an organic solvent were added poly(N,N-dimethylacrylamide/3,3-dimethoxypropene/acrolein) (3g) obtained from Example 1, poly(methylmethacrylate/2-hydroxyethylmethacrylate/acrylic acid) (7g) obtained from Example 2 and triphenylsulfonium triflate (0.05g) as a photoacid generator. The resulting mixture was filtered with a 0.20 $\mu$ m filter, thereby a disclosed photoresist composition.

#### Example 5. Formation of Photoresist Patterns (1)

The photoresist composition obtained from Example 3 was spin-coated on a silicon wafer to form a photoresist film, and baked at 130°C for 90 seconds. After baking, the photoresist film was exposed to light using an ArF exposer of ASML Co. Ltd., and then post-baked at 130°C for 90 seconds. When the post-baking was completed, it was developed in 2.38wt% aqueous TMAH solution for 40 seconds, to obtain 100nm L/S pattern without collapse (see Fig. 2).

#### Example 6. Formation of Photoresist Patterns (2)

The photoresist composition obtained from Example 4 was spin-coated on a silicon wafer to form a photoresist film, and baked at 130°C for 90 seconds. After baking, the photoresist film was exposed to light using an ArF exposer of ASML Co. Ltd., and then post-baked at 130°C for 90 seconds. When the post-baking was completed, it was developed in 2.38wt% aqueous TMAH solution for 40 seconds, to obtain 100nm L/S pattern without collapse (see Fig. 3).

As discussed earlier, ultrafine patterns without collapse are formed by using the disclosed negative photoresist composition containing a photoresist polymer which causes cross-linking reaction by acids generated from exposure. The disclosed photoresist composition is very useful for a photolithography process using EUV for forming patterns of less than 50nm.